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CITATION:

Inouye, Yuzo ...[et al]. Resolution of (±)-trans-3-(trans-2'-Carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic Acid. Bulletin of the Institute for Chemical Research, Kyoto University 1956, 34(1-2): 90-91

ISSUE DATE:

1956-03-30

URL:

http://hdl.handle.net/2433/75538

Resolution of (±)-*trans*-3-(*trans*-2′-Carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic Acid

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Received February 23, 1956

As was described in the previous papers[1], (±)-*trans*-3-(*trans*-2′-carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid, mp. 208°, prepared following our synthetic scheme, was shown to be the racemic form of the naturally derived chrysanthemum-dicarboxylic acid by the identity of their infra-red and ultra-violet absorption spectra, as well as by synthetic and degrative evidence. After the attempts to resolve this racemic acid into diastereoisomers with commoner alkaloids, we have succeeded in obtaining the dextrorotatory acid by means of a synthetic optically active base, α-phenylethylamine.

The (−)-α-phenylethylamine salt of the (+)-acid obtained pure after fractional crystallisation had mp. 224-5° and $[\alpha]_D^{11}$+28.3°, which did not alter on further recrystallisation. Decomposition of this salt by dilute sulphuric acid gave pure crystalline (+)-*trans*-3-(*trans*-2′-carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid, mp. 163-4°, $[\alpha]_D^{11}$+70.9°. The melting point was not depressed when mixed with the naturally derived chrysanthemum-dicarboxylic acid. The complete synthesis of chrysanthemum-dicarboxylic acid was thereby achieved.

In one of our experiments to resolve the racemic acid by means of brucine, the filtrate from the first crop of the brucine salt, when acidified, gave acids with small dextrorotation.

To a boiling solution of this acids (4.1 g.) in 120 ml. of methanol were added 2.5 g. of (−)-α-phenylethylamine, having $[\alpha]_D^{11}$−38.9°, in 10 ml. of methanol. The solution was kept overnight and the first crop of salt (2.6 g.) was separated and the mother liquor evaporated, this procedure being repeated so that five crops were obtained by successive reduction of the volume.

After successive recrystallisations of these crops and combining crops with approximately the same rotation to the first crop and recrystallising the combined salt many times from dilute methanol, there was finally obtained a pure (−)-α-phenylethylamine salt of the (+)-acid (0.7 g.), mp. 224-5°, $[\alpha]_D^{11}$+28.3° (*c*, 1.1, *l*, 1 in methanol). (*Anal.* Found C,67.91, H, 8.06, Calcd. for $C_{18}H_{25}O_4N$, C, 67.69, H, 7.89). Further recrystallisation did not alter these values. Subsequent decomposition of this salt (0.5

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g.) by dilute sulphuric acid gave the pure crystalline (+)-*trans*-3-(*trans*-2′-carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid (0.23 g.), mp. 163-4°, $[\alpha]_D^{11}$+70.9° (*c*, 3.3, *l*, 1 in ethanol), (*Anal.* Found C, 60.54, H, 7.19, Calcd. for $C_{10}H_{14}O_4$, C, 60.59, H, 7.12). The melting point was not depressed when mixed with the naturally derived chrysanthemum-dicarboxylic acid, mp. 164°, $[\alpha]_D^{11}$+71.2° (*c*,1.5, *l*, 1 in ethanol). (cf. Standinger and Ruzicka[2], $[\alpha]_D^{11}$+72.8°). Di-*p*-phenylphenacylester mp. 151-2°, $[\alpha]_D^{11}$+123.3° (*c*, 0.9, *l*, 1 in chloroform), (*Anal.* Found C, 77.51, H, 5.91, Calcd. for $C_{38}H_{34}O_6$ C, 77.79, H, 5.84)

Further resolution by means of (+)-α-phenylethylamine in order to obtain the enantiomorphic laevorotatory acid from the residual salt mixture described above, is now in progress and will be described elsewhere in detail.

The authors are indebted to Prof. S. Takei for his kind advice and to the Ministry of Education for the research grant.

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